Competitive Reactions in the Mechanistic Study of Catalytic Reactions

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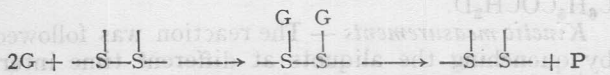
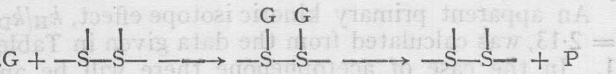
Acetic acid reacts over ferric oxide surface giving acetone, carbon dioxide and water. The use of competitive reaction technique with the esterification of acetic acid with alcohols as the competitive reaction to investigate the mechanistic model — Langmuir-Hinshelwood or Rideal-Eley for ketonization is illustrated.

MOST of the bimolecular catalytic reactions follow the Langmuir-Hinshelwood mechanism[1] where the interaction of two adsorbed species (G-S) takes place giving rise to products (P) as shown below:



However, reactions such as the hydrogenation of olefins and the conversion of *ortho-* and *para-*hydrogens are known to obey a Rideal-Eley mechanism[2,3].



A knowledge of the mechanistic model for heterogeneously catalysed chemical conversions is very useful in the elucidation of the complete mechanism of a particular reaction.

The technique of competitive kinetics[4,5] has been made use of to deduce the mechanism of the surface reaction in the ketonization of acetic acid on iron oxide. The present note reports on the limitations of this technique in determining the order of the surface reaction. The esterification of acetic acid by an alcohol has been chosen as the competing reaction for the ketonization of acetic acid under identical conditions. Studies on the mutual inhibition of the reaction of acetic acid and alcohol indicate that both the molecules compete for the same surface of the catalyst. The rate of formation of ester shows a maximum at a definite partial pressure of acid or alcohol.

If the esterification followed a Langmuir-Hinshelwood mechanism, the rate expression (1) will give at the maximum for ester formation,

$$V = k_{\text{est.}} \frac{b_A p_A \times b_M p_M}{(b_A p_A + b_M p_M)^2} \quad \ldots(1)$$

where

$$\frac{b_A}{b_M} = \frac{p_M}{p_A} \quad \ldots(2)$$

where b and p are the adsorption coefficient and the partial pressure respectively. On the other hand, if the Rideal-Eley mechanism is operative

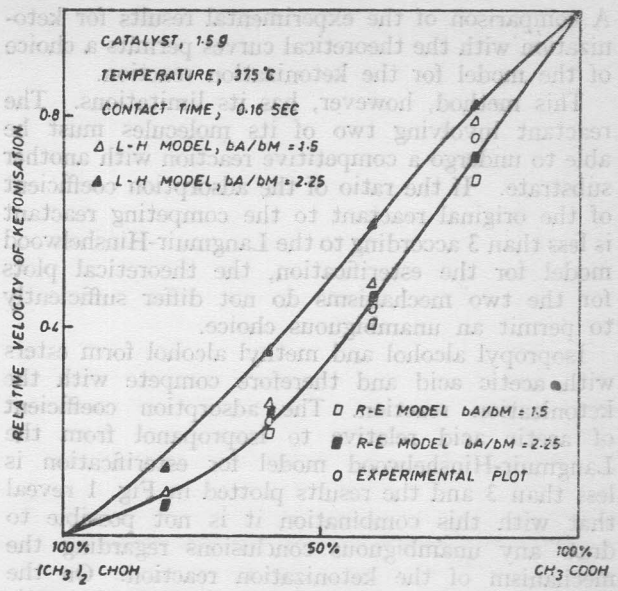


Fig. 1 — Ketonization of isopropanol and Langmuir-Hinshelwood (L-H) and Rideal-Eley (R-E) models

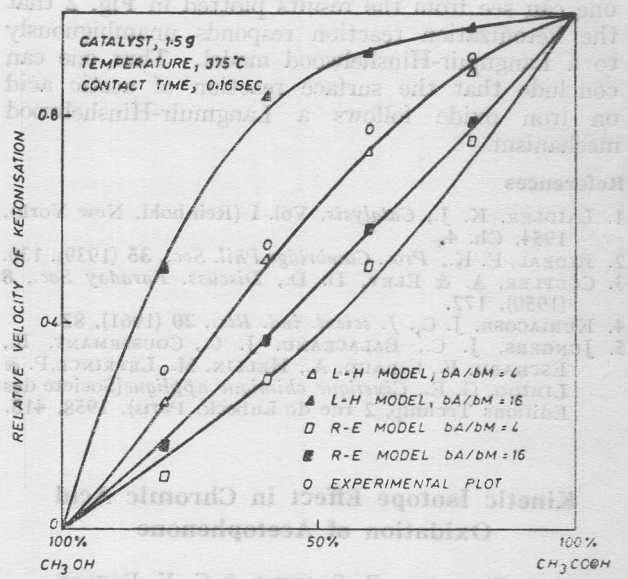


Fig. 2 — Ketonization of methanol and Langmuir-Hinshelwood (L-H) and Rideal-Eley (R-E) models

for the esterification the rate expression (3) provides the condition for maximum as

$$V = k_{\text{est.}} \frac{b_A p_A \times p_M}{b_A p_A + b_M p_M} \text{ or } k_{\text{est.}} \frac{b_M p_M \times p_A}{b_A p_A + b_M p_M} \quad \ldots(3)$$

$$\frac{b_A}{b_M} = \left[\frac{p_M}{p_A}\right]^2 \quad \ldots(4)$$

Now, four theoretical curves can be constructed using the relative values of the adsorption coefficients in the rate expressions 5 and 6 for ketonization.

$$V_i = k_{\text{keton.}} \left[\frac{b_A p_A}{b_A p_A + b_M p_M}\right]^2 \quad \ldots(5)$$

and

$$V_i = k_{\text{keton.}} \frac{b_A p_A^2}{b_A p_A + b_M p_M} \quad \ldots(6)$$

A comparison of the experimental results for ketonization with the theoretical curves permits a choice of the model for the ketonization reaction.

This method, however, has its limitations. The reactant involving two of its molecules must be able to undergo a competitive reaction with another substrate. If the ratio of the adsorption coefficient of the original reactant to the competing reactant is less than 3 according to the Langmuir-Hinshelwood model for the esterification, the theoretical plots for the two mechanisms do not differ sufficiently to permit an unambiguous choice.

Isopropyl alcohol and methyl alcohol form esters with acetic acid and therefore compete with the ketonization reaction. The adsorption coefficient of acetic acid relative to isopropanol from the Langmuir-Hinshelwood model for esterification is less than 3 and the results plotted in Fig. 1 reveal that with this combination it is not possible to draw any unambiguous conclusions regarding the mechanism of the ketonization reaction. On the other hand the adsorption coefficient of acetic acid with respect to methanol is more than 3 and one can see from the results plotted in Fig. 2 that the ketonization reaction responds unambiguously to a Langmuir-Hinshelwood model. Thus one can conclude that the surface reaction of acetic acid on iron oxide follows a Langmuir-Hinshelwood mechanism.

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Kinetic Isotope Effect in Chromic Acid Oxidation of Acetophenone

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The observed kinetic isotope effect (=2·13) in the oxidation of $PhCOCH_3$ and $PhCOCH_2D$ by chromic acid is explained by assuming a primary kinetic isotope effect (=5·0) and secondary kinetic isotope effect (=1·66).

WATERS and coworkers[1] in the oxidation of cyclohexanone by chromic acid have shown that the reaction involves participation of an enol intermediate. Their conclusions are based on the primary kinetic isotope effect $k_H/k_D = 5·0$ and the solvent isotope effect $k_{D_2O}/k_{H_2O} = 4·5$. Participation of the enol intermediate has also been demonstrated by Rocek and Riehl[2] in the chromic acid oxidations of isobutyrophenone and 2-chlorocyclohexanone. We now report in this note our observations on both primary and secondary kinetic isotope effects in the oxidation of acetophenone by chromic acid.

TABLE 1 — RATE CONSTANTS FOR THE CHROMIC ACID AND OXIDATION OF ACETOPHENONE AND ACETOPHENONE-α-*d* AT 50°C {$[Cr(VI)] = 5·5 \times 10^{-3}M$; $[HClO_4] = 4·05M$; $[PhCOCH_3] = 0·102M$; $[PhCOCH_2D] = 0·093M$; solvent: 50% AcOH (v/v)}

Substrate	$k_1^* \times 10^5$ sec^{-1}	$10^3 k_1$/[Ketone] litre mole^{-1} sec^{-1}
$PhCOCH_3$	87·72	8·60
$PhCOCH_2D$	37·61	4·04

*Mean of triplicate runs.

The reagents used were either chemically pure or were purified using conventional methods. Deuterated acetophenone (α-*d*) was prepared by the method of Jones *et al.*[3] PMR analysis showed only 33% deuteration suggesting the formation of $C_6H_5COCH_2D$.

Kinetic measurements — The reaction was followed by quenching the aliquots at different time intervals with a slight excess of acidified ferrous ammonium sulfate (AR grade) solution and then estimating titrimetrically the ferrous ions, left unreacted against standard $K_2Cr_2O_7$ using barium diphenylamine sulphonate as the indicator.

An apparent primary kinetic isotope effect, $k_H/k_D = 2·13$, was calculated from the data given in Table 1. In the case of acetophenone there will be an statistical effect in the sense that removal of the three hydrogen atoms of $-CH_3$ group is equally possible. However, in the case of deuterated analogue the rate would include the possibility of removal of H as well as D from $-CH_2D$ group. But the probability of removal of H is twice that of D. Further because of the presence of C-D bond, the rate at which C-H fission would take place in the deuterated sample will be less than that for C-H fission in acetophenone (secondary kinetic isotope effect k_H/k_H^1). The rate of oxidation of dueterated acetophenone would, therefore, be equal to $2k_H^1 + k_D$, as shown below:

$$PhCOCH_3 \xrightarrow{3k_H} PhCOCH_2OH$$

$$PhCOCH_2D \xrightarrow{2k_H^1 \text{ or } k_D} PhCOCHD(OH)$$

In the case of chromic acid oxidation of cyclohexanone, Waters and coworkers[1] have reported the value of primary kinetic isotope effect k_H/k_D to be equal to 4-5. Assuming $k_H/k_D = 5$ in the present case also, one can calculate the secondary kinetic isotope effect $k_H/k_H^1 = 1·66$ from the relation:

$$3k_H/(2k_H^1 + k_D) = 8·6/4·04 = 2·13$$

A secondary kinetic isotope effect of this magnitude has also been reported by Bell[4]. Thus the observed rate of chromic acid oxidation of $PhCOCH_2D$